Redox Chemistry of Ruthenium Porphyrins: Evidence for Internal Electron Transfer and the Characterization of $[Ru^{III}(OEP^{+\cdot})]$ Species

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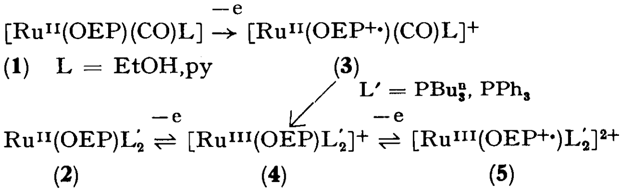
Summary An internal electron transfer process from ruthenium(II) to an octaethylporphyrin radical moiety is induced by changes in axial ligation, and the species formed by a two-electron oxidation of ruthenium(II) porphyrins is characterized as a ruthenium(III) porphyrin cation radical.

ALTHOUGH the redox properties of metalloporphyrins have been studied extensively, data on ruthenium porphyrins have been confined to $[Ru^{II}(porphyrin)(CO)L]$ (**1**) and $[Ru^{II}(porphyrin)L_2]$ (**2**) complexes, L = py, MeCN, tetrahydrofuran, PR_3; porphyrin = dianion of octaethylporphyrin (OEP) or *meso*-tetraphenylporphyrin (TPP).[1–3] The one-electron electrochemical oxidation of (**2**) occurs at the metal, as judged usually by visible spectral data and lack of an e.s.r. signal attributable to the porphyrin cation radical, although recently with some chemically oxidized systems, L = PBu^n_3 or PPh_3, we have successfully observed e.s.r. signals to 77 K attributable to the low-spin Ru^{III} centre and have isolated the $[Ru^{III}(OEP)(PBu^n_3)_2]^+Br^-$ complex.[4] Oxidation of the monocarbonyl complexes (**1**) occurs at the porphyrin ring to give a π-cation radical species (**3**).[5] In this communication we report a change in oxidation site *via* a presumed internal electron transfer process [(**3**) → (**4**)] and detection of $[Ru^{III}(OEP^{+\cdot})]^{2+}$ (**5**) formed by the two-electron oxidation of ruthenium(II) porphyrin complexes.



$$\begin{tikzcd}[Ru^{II}(OEP)(CO)L] \arrow[r, "-e"] & {[Ru^{II}(OEP^{+\cdot})(CO)L]^+} \arrow[dl, "L' = PBu^n_3,\ PPh_3"] & \\ Ru^{II}(OEP)L'_2 \arrow[r, "-e", shift left] & {[Ru^{III}(OEP)L'_2]^+} \arrow[l, shift left] \arrow[r, "-e", shift left] & {[Ru^{III}(OEP^{+\cdot})L'_2]^{2+}} \arrow[l, shift left]\end{tikzcd}$$

(**1**) L = EtOH,py (**3**) (**2**) (**4**) (**5**)

SCHEME

The Table lists electronic spectral data for the various species. Solutions of the cation radical species (**3**) generated from (**1**) electrochemically (**3a**)[5] or *via* Br_2-oxidation (**3b**), react with ⩾2 equiv. of tertiary phosphine to yield (**4**), which can also be formed electrochemically in a reversible manner, from authentic samples of (**2**), for example, $E_{\frac{1}{2}}$ = *ca.* 0·0 V (*vs.* Ag/AgCl) for L′ = PBu^n_3 (Figure). Clean spectral changes with several isosbestic points are observed in CH_2Cl_2 for the (**2**) ⇌ (**4**) electrochemical conversions consistent with no ligand exchange reactions. The cyclic

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TABLE. U.v./vis. spectroscopic data for [Ru(OEP)] species.

Complex	λ_{max}/nm (log ϵ)
(**3a**)[a]	587 (3·76), 535 (3·7), 375 (4·8)
(**3b**)[a]	628 (3·8), 575 (3·6), 385 (4·6)
(**4**), L′ = PBu^{n}_{3}	790 (3·52), 516 (3·95), 410 (4·65), 363 (4·72)
(**2**), L′ = PBu^{n}_{3}	535 (4·04), 511 (4·2), 428 (5·27), 416 (4·66), 360 (4·65)
(**5**), L′ = PBu^{n}_{3}	790 (3·0), 510 (4·0), 363 (4·9)

[a] Differences result from anions present: ClO_4^- (from $Bu_4N^+ClO_4^-$) in electrochemical method (**3a**); Br^- from a Br_2-oxidation (**3b**). The nature of L in (**3**) is thus uncertain; the [Ru(OEP)(CO)py] system behaves similarly giving purple (**3a**) or green (**3b**) solutions depending upon the method of oxidation.

voltammogram of (**4**; L′ = PBu^{n}_{3}) shows a second quasi-reversible wave at higher potentials that we attribute to formation of the Ru^{III} π-cation radical, (**4**) $\rightleftharpoons$ (**5**); addition of MeCN shifts the E_p values, particularly for the second wave, to less positive potentials, due presumably to enhanced stabilization of the positively charged species in the more polar media. The lack of peak broadening or new waves, and an i_{pc}/i_{pa} ratio of unity, again indicate no ligand exchange.[6]

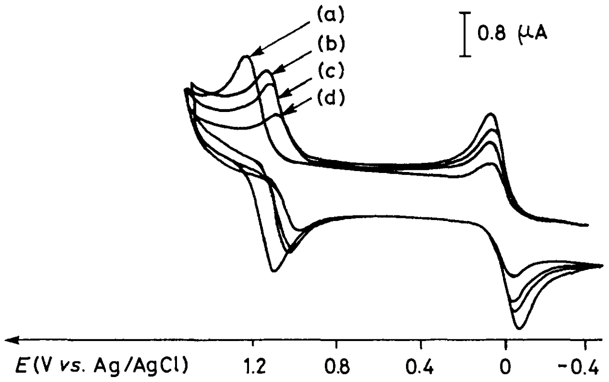

FIGURE. Cyclic voltammogram of species (**2**), L = PBu^{n}_{3}, using $Bu_4N^+ClO_4^-$ as electrolyte and a Pt anode (scan rate 250 mV/s): (a) in CH_2Cl_2; (b) in CH_2Cl_2–MeCN (3:1, v/v); (c) CH_2Cl_2–MeCN (1:1); (d) CH_2Cl_2–MeCN (1:2).

Acetonitrile solutions of (**5**; L′ = PBu^{n}_{3}) at 77 K show a broad e.s.r. signal at g_{av} = 2·35 (half peak width 80 G), attributable to low-spin Ru^{III},[4,7] and a sharp g_{av} = 2.008 cation radical-like signal (peak-to-peak width 10 G); integration of the two peaks shows approximately equal areas. Thus there appears to be no coupling between the paramagnetic centres of species (**5**), although on increasing the temperature to 200 K the broad signal is lost and the narrow signal is reduced markedly in intensity. On warming to room temperature, the MeCN solutions of (**5**) decompose slowly to generate $[\mathrm{Ru}^{III}(\mathrm{OEP})(\mathrm{MeCN})_2]^+$, although (**4**; L′ = PBu^{n}_{3}) is recovered following electrochemical reduction back to the divalent stage.

It has been suggested previously that a similar internal electron transfer within the $[\mathrm{Ni}^{II}(\mathrm{TPP}^{+\bullet})]^+ \rightleftharpoons [\mathrm{Ni}^{III}(\mathrm{TPP})]^+$ system might be controlled by axial ligation[8] and the present studies support this hypothesis. Porphyrin π-cation radicals appear to play key roles in electron transfer processes within a variety of heme proteins.[9] Recent evidence suggests that the intermediate in some cytochrome P-450 systems responsible for hydrocarbon oxidations may also be a porphyrin π-cation radical.[10] The detection of the second-row dicationic species (**5**), and the axial ligand-induced redox process shown in the Scheme should allow for more detailed study of these important internal electron transfer reactions between the metal and porphyrin.

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